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An approach to elucidating photocatalytic reaction mechanisms by monitoring dissolved oxygen: Effect of H_2O_2 on photocatalysis

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ABSTRACT

We present a method to analyze the photocatalytic oxidation of ethanol (EtOH) in an aqueous TiO_2 suspension by measuring the consumption of dissolved oxygen (DO) as a function of varying EtOH and H_2O_2 concentrations in the suspension. The consumption of DO was analyzed by means of Langmuir–Hinshelwood (L–H) kinetics. The parameter $K_{D\text{-}DO}$ calculated from L–H kinetics, defined as (O_2 consumption rate constant) (O_2 reproduction rate constant)$^{-1}$, reflects the adsorption equilibrium of EtOH and the photocatalytic reaction mechanisms. The observed $K_{D\text{-}DO}$ values for the photocatalytic oxidation of EtOH reflected to the proposed reaction mechanism measured by HPLC and starch–Iodine methods. By using this DO analysis method, we elucidated the photocatalytic reaction mechanism of EtOH oxidation and discussed the effect of H_2O_2 as active oxygen species on TiO_2 photocatalysis.

1. Introduction

TiO_2 photocatalysis is a commonly used method for the decomposition and mineralization of environmental pollutants and other undesirable compounds [1]. Molecular oxygen (O_2) is consumed in the reaction, and the O_2 consumption has been studied in the context of O_2 "photo-adsorption" and water splitting [2,3]. Studies of the role of O_2 have revealed that the reaction actually proceeds by the simultaneous reduction and oxidation of O_2 [4].

Oxygen has three important roles in photocatalysis [5–24]. First, the reduction of O_2 improves the photocatalytic activity to promote electron–hole (e^-–h^+) charge separation [5–7]. Second, O_2 accepts electrons generated in TiO_2 and is reduced to $O_2^{\bullet-}$, H_2O_2, OH radicals, and Ti–O$^\bullet$ (or Ti-$^\bullet$OH). These surface-active species promote the photocatalytic oxidation of organic compounds [5–11]. Finally, upon oxidation, O_2 combines with organic radicals, which are generated by the reaction of holes with the reactant, to produce oxygen adduct intermediates such as organoperoxy radicals (ROO$^\bullet$) [12–24]. These intermediates are mineralized to CO_2 and H_2O by consuming O_2. Hence, O_2 is an indispensable molecule in photocatalytic reaction pathways, as represented in Scheme 1.

Thus far, the roles of O_2 in photocatalysis have been studied mainly by means of water splitting, ESR measurement for observing producing $O_2^{\bullet-}$ and Ti^{3+} disappearing and a decomposition of organic compounds as an effect of oxygen and by analysis of O_2 reduction processes on TiO_2/polymer hybrid films [2,25–28]. A technique known as the chemical oxygen demand test, which is based on measuring oxygen consumption in TiO_2 photocatalysis, has recently been developed to estimate water pollution [29,30]. On the other hands, we reported at first time the utilization of O_2 to estimate photocatalytic activity by analyzing the oxygen decay process [31]. In the estimation, ethanol (EtOH) and iso-propanol (i-PrOH) are employed as standard compounds because these alcohols are completely decomposed to CO_2 and H_2O through a well-studied, oxygen-assisted photocatalytic mineralization [11–24].

Many intermediate species are produced in the photocatalytic reaction process, including oxygenated intermediates that may be further oxidized to H_2O and CO_2 [11–21]. Large amounts of $O_2^{\bullet-}$ and H_2O_2 are also produced in TiO_2 photocatalysis, and the generated H_2O_2 is reduced and oxidized to OH radicals and $O_2^{\bullet-}$. In this way, H_2O_2 is decomposed to H_2O and O_2 through organic compound mineralization [5–10,21]. Therefore, we can assume that H_2O_2 is one of the intermediate from the viewpoint of O_2 in the TiO_2-photocatalyzed mineralization of organic compounds. Reactions involving H_2O_2 are also represented in Scheme 1.

Since O_2 consumption and CO_2 production occur simultaneously in TiO_2-photocatalyzed decomposition of organic compounds, we strongly suspected that the decomposition mechanism for TiO_2 photocatalysis could be elucidated by monitoring the behavior of O_2. However, such a study had never been carried out.

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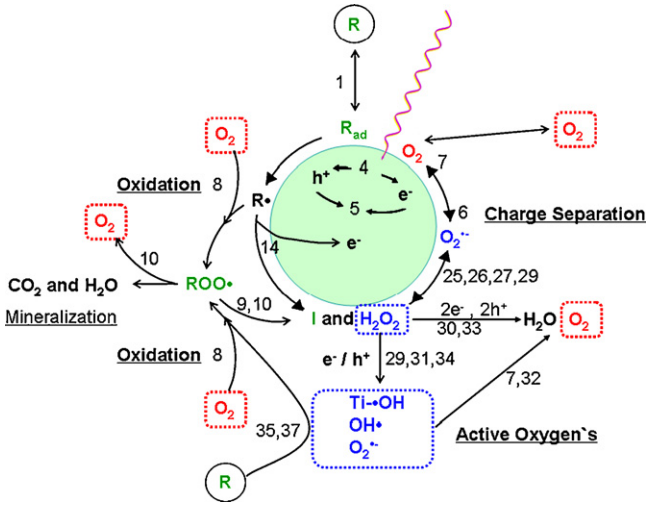


Scheme 1. Photocatalytic reaction mechanism for O_2-assisted decomposition of organic compounds at $TiO_2^{\bullet}$, R, R_{ad} and ROO• are the organic reactant, adsorbed reactant and oxygenated reactant intermediate, respectively.

In the present study, we attempt to quantitatively and kinetically analyze EtOH oxidation in a TiO_2 photocatalytic system by monitoring both behavior of dissolved oxygen (DO) and H_2O_2. We used EtOH as the model organic compound in the present study because its reaction mechanism has been widely studied, as represented in Scheme 2 [12–19].

2. Experimental

2.1. Materials

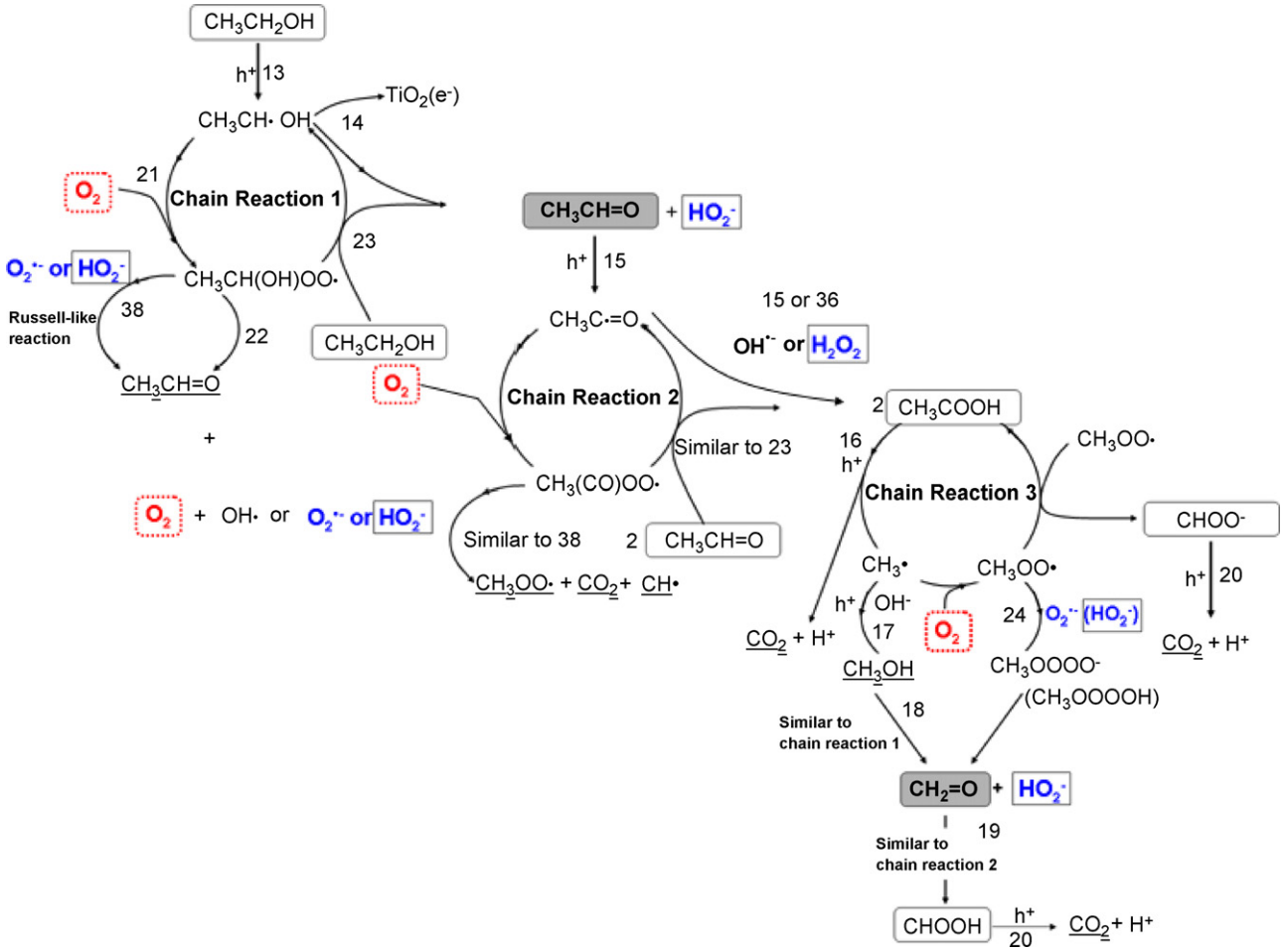
TiO_2 powder (P25, Nippon aerojil) was used as a photocatalyst. A thin layer of P25 TiO_2 was placed on glass and exposed to UV light (SANKYO DENKI BLB Hg Lamp) at 354 nm for 120 h under ambient to completely decompose any surface pollutants. The UV-treated P25 powder was stored in a glass bottle in the dark. The complete decomposition of surface pollutants was estimated by stopping dissolved oxygen (DO) consumption in suspension [31,32]. Distilled water for HPLC (Wako) was used to prepare an TiO_2 suspension. Ethanol (Wako, 99.5%), acetaldehyde (Wako, 95%) and formaldehyde (SIGMA, 37%; contains 10–15% methanol) were used without further purification.

2.2. Analytical methods

2.2.1. Monitoring consumption of dissolved oxygen

The behavior of DO during photocatalysis of the TiO_2 suspension was monitored with electrode for DO sensor (UC-12-SOL, Central Kagaku Co.), which was connected to a computer. A 100 mL colorimetric bottle (As-one) was used to effectively irradiate the TiO_2 suspension with UV light.

For DO monitoring, a TiO_2 suspension was prepared in 100 mL of 0.01 M NaOH, and the suspension was agitated by ultrasonic for 10 min. After agitation, the suspension was transferred to the colorimetric bottle and a known concentration of EtOH was added,



Scheme 2. Photocatalytic reaction mechanism for O_2-assisted ethanol decomposition. $CH_3C{=}O$, $CH_2{=}O$, H_2O_2, $O_2^{\bullet-}$, and O_2 were measured in this study.

and was stirred vigorously for 30 min under ambient to establish DO equilibrium within the suspension. The electrode for DO sensor was then immersed in the suspension, and the bottle was sealed with a Teflon or silicon cap. The suspension filled the bottle completely so that there was no space for air in the system. The suspension was stirred vigorously during experiments. UV irradiation was carried out with four black light bulbs (FL10B, Toshiba). The light intensity was measured with a photometer (UV Caremate Pro, Fuji Xerox) and was 2.7 mW cm^{-2} inside the bottle. The temperature of the suspension was maintained at 295 K by directing a fan toward the bottle to prevent temperature increases. Other details for these DO measurements have been described elsewhere [31].

2.2.2. Analysis of acetaldehyde and formaldehyde

The acetaldehyde and formaldehyde generated from photocatalysis with EtOH were measured by HPLC (Shimadzu LC-10AT) equipped with a photodiode array detector (Shimadzu) [33]. Experimental concentrations of acetaldehyde and formaldehyde were estimated by fitting experimental data to calibration curves of known acetaldehyde and formaldehyde concentrations. After photocatalysis, the TiO_2 suspension was filtered through a 0.2 μm polypropylene disposable filter (Whatman), and the pH of the supernatant was adjusted to 2 with 1 M HNO_3. The supernatant was added to acetonitrile containing 2,4-dinitrophenylhydrazine (2,4-DNPH) to form the 2,4-DNPH derivatives of the aldehydes.

2.2.3. Analysis of H_2O_2

The amount of H_2O_2 photocatalytically produced was estimated by the starch–Iodine method. Before the addition of I^- and starch, the TiO_2 suspension was filtered and the supernatant pH was adjusted as described in Section 2.2.2. After addition of I^- and starch, the solution was kept in the dark for 5 min in order to finish the reaction. The absorption at I^{3-} was measured with the UV-vis-NIR spectrometer (UV-3600 Shimadzu). The experimental concentration of H_2O_2 was estimated by fitting the experimental data to a calibration curve constructed from known concentrations of H_2O_2.

2.3. The parameter obtained from L–H kinetics for DO consumption

In Langmuir–Hinshelwood (L–H) kinetics, the maximum DO consumption rate (r_{max}) and the equilibrium constant (K_D) for the adsorption reaction

$$TiO_2 + R \leftrightarrow TiO_2{-}R_{ad} \quad (1)$$

are calculated by plotting the inverse of the DO decay rate (r_{DO}) against the inverse of the reactant concentration [R]:

$$\frac{1}{r_{DO}} = \frac{1}{r_{max}} + \frac{1}{r_{max}K_D[R]} \quad (2)$$

When the adsorption sites are fully occupied by reactant molecules, r_{max} is equivalent to r_{DO}. The other details of the r_{max} and L–H kinetics for DO consumption are described in our previous report [31]. The equilibrium constant K_D is given by the ratio of the rate constants for adsorption and desorption of reactant R at the TiO_2 surface, $K_D = k_1 k_{-1}^{-1}$, or

$$K_D = \frac{[TiO_2{-}R_{ad}]}{[TiO_2] \times [R]} \quad (3)$$

In TiO_2 photocatalysis, the reactant adsorbed at the TiO_2 surface (R_{ad}) is oxidized to other intermediates and CO_2 by consuming and reproducing O_2, as shown in the following equations:

$$TiO_2{-}R_{ad} + h\nu \rightarrow TiO_2{-}R_{ad}\,(e^- + h^+) \quad (4)$$

$$TiO_2{-}R_{ad}\,(e^- + h^+) \rightarrow TiO_2{-}R_{ad}\,(\text{heat}) \quad (5)$$

$$TiO_2{-}R_{ad}\,(e^-) + O_2 \rightarrow TiO_2{-}R_{ad} + O_2^{\bullet -} \quad (6)$$

$$TiO_2{-}R_{ad}\,(h^+) + O_2^{\bullet -} \rightarrow TiO_2{-}R_{ad} + O_2 \quad (7)$$

$$TiO_2{-}R_{ad}\,(h^+) + O_2\,(\text{or} + O_2^{\bullet -}) \rightarrow TiO_2{-}ROO^{\bullet} \quad (8)$$

$$TiO_2{-}ROO^{\bullet} \rightarrow TiO_2{-}I + CO_2 \quad (9)$$

$$TiO_2{-}ROO^{\bullet} \rightarrow TiO_2{-}I + O_2 \quad (10)$$

In these equations, $ROO^{\bullet}$ and I represent intermediates and oxygenated radical intermediates. We assumed that the K_D values observed in this study reflected both the adsorption and desorption of O_2 [31]. Therefore, K_D for O_2 consumption in our TiO_2 photocatalysis can be defined as the reaction equilibrium for the consumption and reproduction of O_2 ($K_{D\text{-}DO}$), as shown in the following equation:

$$K_{D\text{-}DO} = [TiO_2{-}R_{ad}{-}O_2]\,([TiO_2{-}R_{ad}][O_2])^{-1} \quad (11)$$

$K_{D\text{-}DO}$ is also represented by Eq. (12), which demonstrates the adsorption equilibrium of R and the photocatalytic reaction mechanism through rates of O_2 consumption and reproduction [31]:

$$K_{D\text{-}DO} = (O_2 \text{ consumption rate constant})\,(O_2 \text{ reproduction rate constant})^{-1} \quad (12)$$

Since a large $K_{D\text{-}DO}$ value is attributable to the irreversible reaction to consume DO, a large observed $K_{D\text{-}DO}$ should indicate more efficient photocatalytic mineralization. According to the definition of the reaction (12), varying $K_{D\text{-}DO}$ values reflect a proceeding the varying photocatalytic reaction.

3. Results

3.1. Dependency of ethanol concentration on DO consumption

Fig. 1 shows DO decay during the photocatalytic oxidation of varying concentrations of EtOH. The DO decay rate, r_{DO}, increased with increasing concentrations of EtOH. When the EtOH concentration was 5 mM, the DO was completely consumed within 20 min of UV irradiation. The DO decay process obeyed zero-order reaction kinetics (i.e., the decay rate was constant), indicating that the DO consumption in this experimental condition was a light intensity limiting reaction [31].

In Fig. 2(a), r_{DO} was plotted as a function of EtOH concentration and was apparently obeyed isothermal lines. However, because the reciprocal plot had two steps near 5 mM of EtOH as shown in Fig. 2(b), the data could not be analyzed by simple L–H kinetics. Instead, the data were divided into low (<5 mM) and high (>5 mM) EtOH concentration ranges, and each of the two ranges was independently fitted by Eq. (2), as shown in Fig. 3. Values of r_{max} and $K_{D\text{-}DO}$ were then calculated from the plots in Fig. 3. The r_{max} and $K_{D\text{-}DO}$ obtained were 11.9 μM min^{-1} and 5610 M^{-1}, respectively, in the low EtOH concentration range and 21 μM min^{-1} and 452 M^{-1}, respectively, in the high EtOH concentration range. These calculated parameters were used to fit the data shown in the inset of Fig. 2(a), and the resulting fits suggest that the data obeyed L–H kinetics for all EtOH concentrations studied. These results indicate that the reaction mechanism is changed at each concentration range of EtOH.

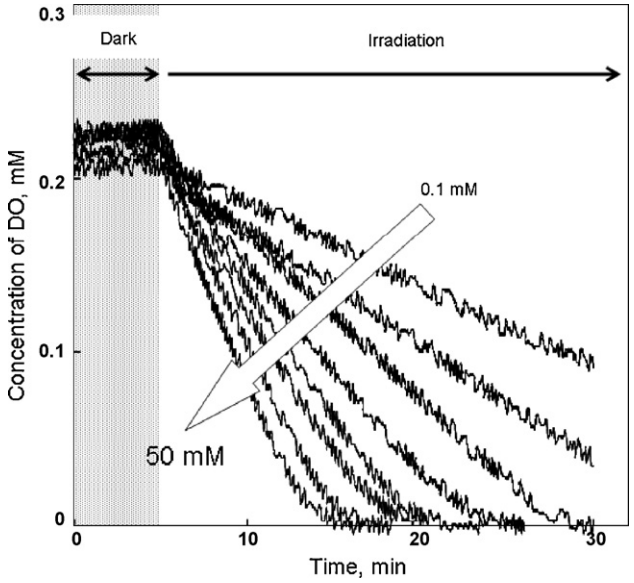


Fig. 1. DO consumption during TiO_2 photocatalysis in an aqueous suspension containing EtOH at concentrations between 0.1 and 50 mM. TiO_2 powder (P25, 0.1 g L^{-1}) was suspended in 0.01 M NaOH (pH 11.5) and stirred in the dark for 5 min prior to UV irradiation.

3.2. Production of acetaldehyde and formaldehyde as intermediates

As stated above, the DO consumption during photocatalysis varied with EtOH concentration. Therefore, we expected that the amounts of major intermediate molecules produced from EtOH oxidation, such as acetaldehyde and formaldehyde, also varied with EtOH concentration as represented in Scheme 2 [34]. To verify this hypothesis, we measured the acetaldehyde and formaldehyde generated during photocatalysis. The UV-irradiation was ceased at 25 min or when DO was completely consumed.

Fig. 4 shows the concentrations of acetaldehyde (◇) and formaldehyde (○) produced as a function of EtOH concentration. The concentration of acetaldehyde increased with increasing EtOH concentration, with the rate of increase slowing substantially at concentrations higher than 1 mM. By contrast, the concentration of generated formaldehyde reached a maximum at 1 mM EtOH and decreased above this EtOH concentration.

The proposed mechanism for photocatalytic oxidation of EtOH is shown in the following equations [11–19]:

$$CH_3CH_2\text{-}OH + h^+ \rightarrow CH_3C^{\bullet}HO + H^+ \quad (13)$$

$$CH_3C^{\bullet}HO + TiO_2 \rightarrow CH_3CH{=}O + TiO_2\,(e^-) \quad (14)$$

$$CH_3CH{=}O + h^+ + OH^- \rightarrow CH_3COOH + H^+ \quad (15)$$

$$CH_3COOH + h^+ \rightarrow CH_3^{\bullet} + CO_2 + H^+ \quad (16)$$

$$CH_3^{\bullet} + OH^- + h^+ \rightarrow CH_3OH \quad (17)$$

$$CH_3OH + h^+ \rightarrow CH_2{=}O + H^+ \quad (18)$$

$$CH_2{=}O + h^+ + OH^- \rightarrow HCOOH + H^+ \quad (19)$$

$$HCOOH + h^+ \rightarrow CO_2 + 2H^+ \quad (20)$$

As shown by these equations, both acetaldehyde and formaldehyde are produced through the photocatalytic oxidation of EtOH. The observed decrease in formaldehyde at EtOH concentrations above 1 mM might be explained by considering that Eq. (15) are inhibited by the Eqs. (13) and (14), indicating that the photocatalytic reaction mechanism varied with EtOH concentration, as described in Section 3.1.

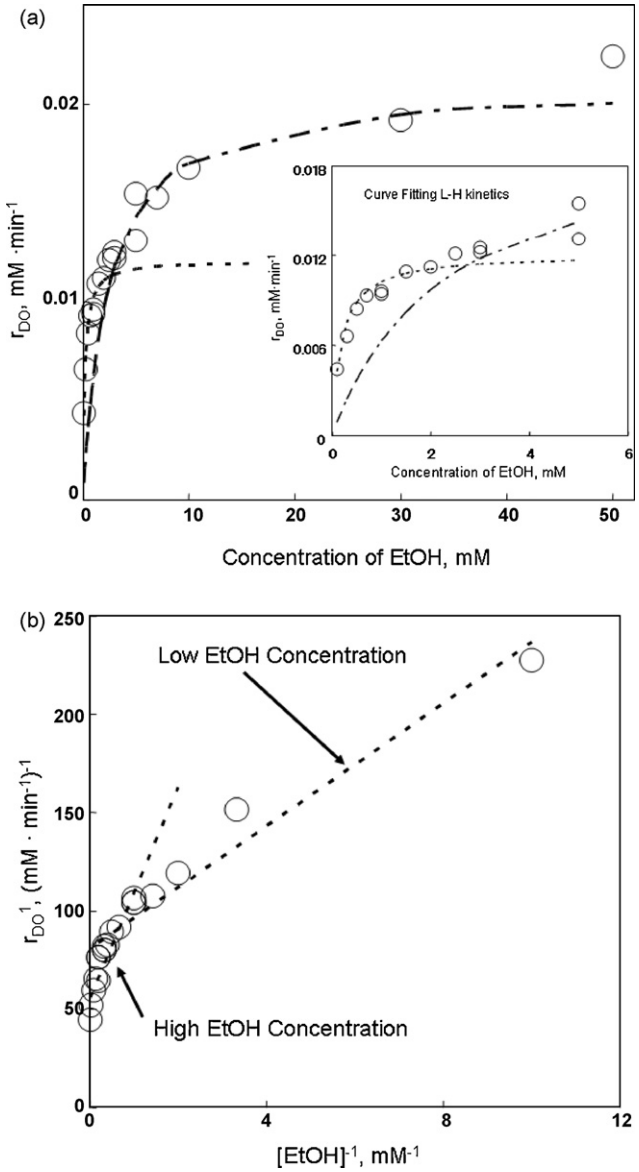


Fig. 2. (a) r_{DO} plotted as a function of EtOH concentration. Inset shows curve fitting using r_{max} and $K_{D\text{-}DO}$ values obtained from L–H analysis of the data (shown in Fig. 3(a)). (b) $1/r_{DO}$ plotted as a function of $[EtOH]^{-1}$.

3.3. H_2O_2 production

In TiO_2 photocatalysis of EtOH, H_2O_2 is one of the intermediate molecules, indicating that H_2O_2 strongly affects the photocatalytic reaction. To verify the dependence of these parameters upon H_2O_2 concentration, we measured the production of H_2O_2 during photocatalytic oxidation of varying concentrations of EtOH. The UV-irradiation was ceased at 25 min or when DO was completely consumed.

Fig. 5 shows the concentration of H_2O_2 produced as a function EtOH concentration. The absorbance at 360 nm attributable to I^{3-} could not be recognized above 5 mM EtOH because of the broad absorption. It might attributable to an products formed by interfering with the reaction of H_2O_2, starch, and I^- to produce

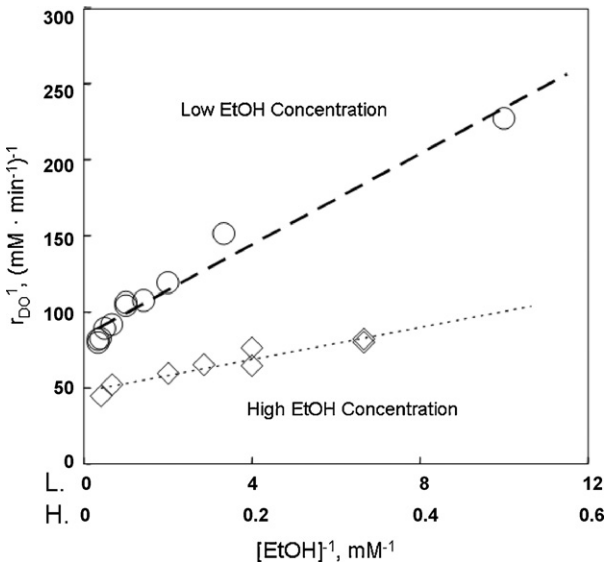


Fig. 3. $1/r_{DO}$ plotted as a function of 1/[EtOH], in which the EtOH concentrations were separated into low (<5 mM) and high (>5 mM) ranges and subjected to L–H analysis.

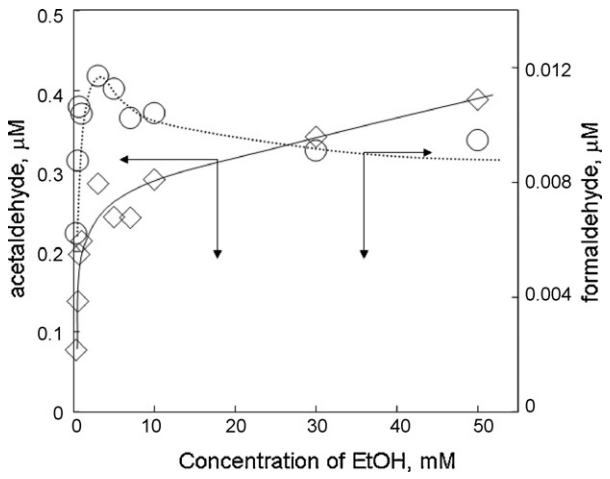


Fig. 4. Concentrations of acetaldehyde (◇) and formaldehyde (○) produced from the photocatalytic oxidation of EtOH at varying concentrations.

I^{3-} with EtOH and an intermediates [35]. The concentration of H_2O_2 produced was much higher than that of acetaldehyde or formaldehyde (Fig. 4). The H_2O_2 concentration increased with increasing EtOH concentration, reaching a maximum of 5 μM H_2O_2 at 1 mM EtOH. In the present study, since every experiment was carried out in closed system, the production of H_2O_2 was stopped when all DO was consumed. Notably, no H_2O_2 was detected in the absence of EtOH by the starch–Iodine method.

H_2O_2 is produced from the equations below [36]:

$$CH_3CH^{\bullet}OH + O_2 \rightarrow CH_3CH^{\bullet}(OH)\,OO \quad (21)$$

$$CH_3CH^{\bullet}(OH)\,OO \rightarrow CH_3CH{=}O + HO_2^- \quad (22)$$

$$CH_3CH^{\bullet}(OH)\,OO + CH_3CH_2\text{-}OH \rightarrow CH_3CH{=}O + CH_3CH^{\bullet}OH + H_2O_2 \quad (23)$$

$$CH_3^{\bullet} + e^- + 2O_2 + H^+ \rightarrow CH_2{=}O + HO_2^- + OH^- \quad (24)$$

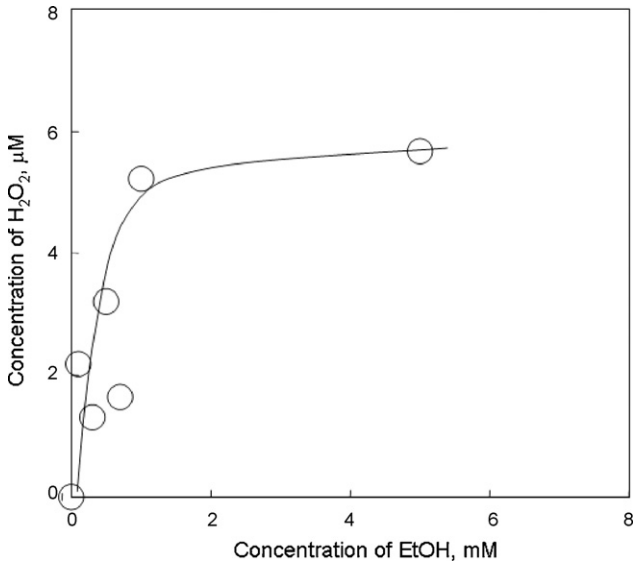


Fig. 5. Concentration of H_2O_2 produced from the photocatalytic oxidation of EtOH at varying concentrations.

$$O_2^{\bullet-} + O_2^{\bullet-} + H^+ \rightarrow HO_2^- + O_2 \quad (25)$$

$$O_2^{\bullet-} + e^- + H^+ \rightarrow HO_2^- \quad (26)$$

$$O_2 + 2e^- + H^+ \rightarrow HO_2^- \quad (27)$$

$$HO_2^- + H^+ \leftrightarrow H_2O_2 \quad (pK_a = 11.7) \quad (28)$$

Eqs. (21)–(23) describe a well-known chain reaction for EtOH oxidation and subsequent acetaldehyde and H_2O_2 production [13–15] and Eq. (24) is also suggested as production rout through Eq. (16). Since the chain reaction is accelerated by the progress of the photocatalytic oxidation of EtOH (Eqs. (13)–(20)) as represented in Scheme 2, which inhibits charge recombination (Eq. (5)), the reaction in Eq. (6) is accelerated and large amounts of H_2O_2 are produced through the reactions in Eqs. (25)–(27) [37–42].

3.4. Effect of H_2O_2 addition on r_{DO} and $K_{D\text{-}DO}$

As seen in Fig. 5, a large amount of H_2O_2 was produced by TiO_2 photocatalysis with EtOH. However, determining the specific effect of H_2O_2 on the photocatalysis process was difficult. To determine the effects of H_2O_2 on the EtOH oxidation and DO consumption, we estimated r_{DO} and $K_{D\text{-}DO}$ from photocatalysis reactions using varying known concentrations of H_2O_2.

Fig. 6 shows the DO decay for TiO_2 photocatalysis with 0.1 mM of H_2O_2 added to the TiO_2 suspension. At low EtOH concentrations (Fig. 6(a)), an increase in the DO concentration was immediately observed upon UV irradiation of the suspension. This observation may reflect the production of O_2 from H_2O_2 oxidized by h^+ (Eqs. (29), (30) and (7)) [5,7–9,37–43]:

$$HO_2^- + h^+ + OH^- \rightarrow O_2^{\bullet-} + H_2O \quad (29)$$

$$HO_2^- + 2h^+ \rightarrow O_2 + H^+ \quad (30)$$

This initial increase in DO upon UV irradiation diminished with increasing concentrations of EtOH, and at 7 mM EtOH, no initial increase was observed (Fig. 6(b)). Furthermore, the starting point for DO consumption was delayed by the addition of H_2O_2 as seen in Fig. 7, suggesting the oxidation of EtOH by TiO_2 photocatalysis

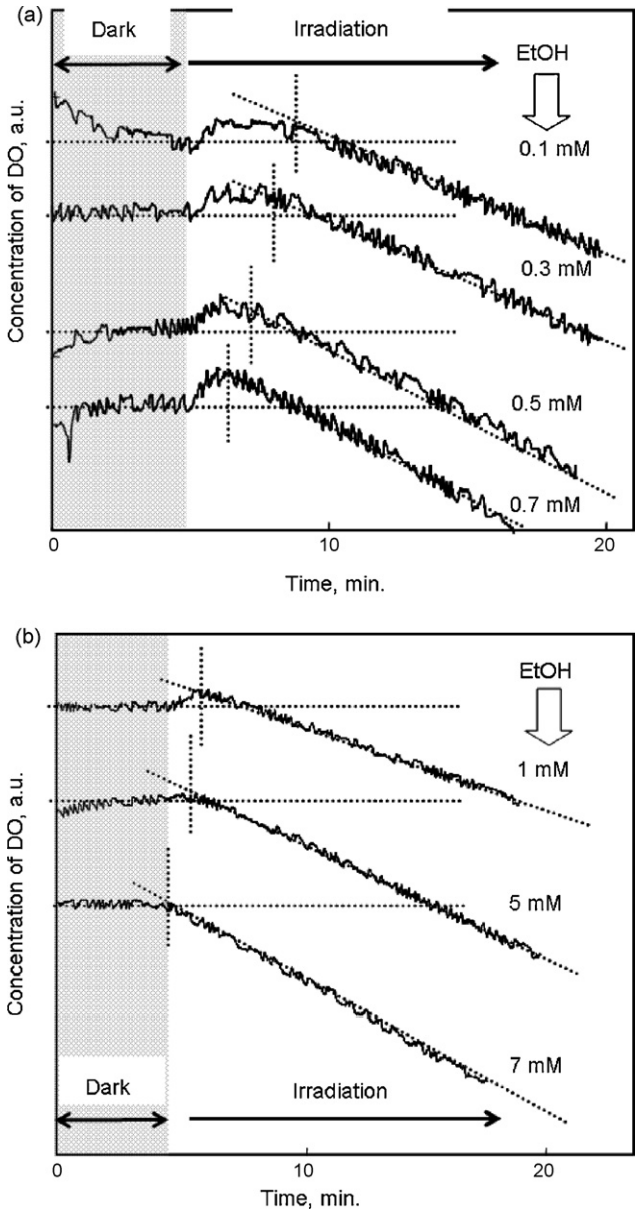


Fig. 6. DO concentration observed during photocatalysis of TiO_2 suspensions containing 0.1 mM of previously added H_2O_2 and several concentrations of EtOH: (a) 0.1–0.7 mM and (b) 1–7 mM.

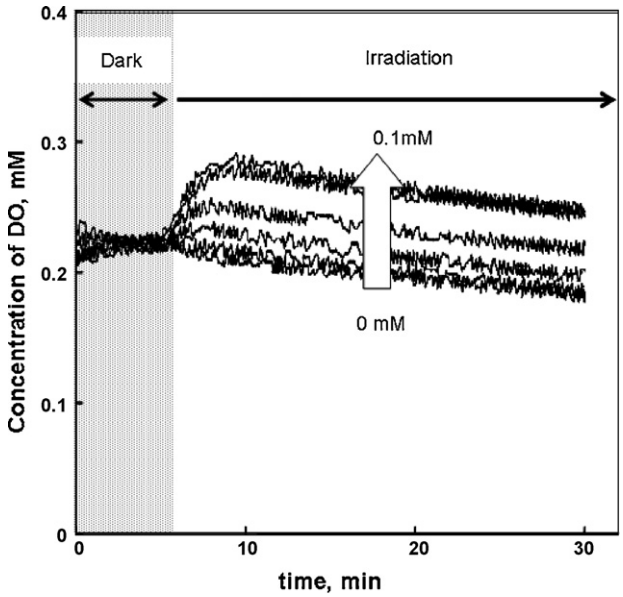


Fig. 7. DO concentration observed during photocatalysis of TiO_2 suspensions containing 0.01–0.1 mM H_2O_2.

(Eq. (13)) competed with oxidation of H_2O_2 by h^+ to produce O_2 (Eqs. (29), (30) and (7)) [44].

The r_{max} of H_2O_2 addition was also divided into two EtOH concentration ranges (not shown here), as described for Fig. 3, using 5 mM EtOH as a boundary point. Then, r_{max} and $K_{D\text{-}DO}$ for L–H kinetics were calculated as 9.7 μM min^{-1} and 11,462 M^{-1}, respectively, for the low EtOH concentration range and 21 μM min^{-1} and 428 M^{-1}, respectively, for the high EtOH concentration range. The obtained r_{max} decreased upon addition of H_2O_2 because the oxidation of H_2O_2 (Eqs. (29), (30) and (7)) competed with EtOH oxidation (Eqs. (13–20)). Furthermore, the $K_{D\text{-}DO}$ value for the low EtOH concentration range was increased by the addition of H_2O_2, indicating that the oxidation of EtOH by photocatalysis was accelerated and that an irreversible reaction resulting in the consumption of DO occurred. By contrast, r_{max} and $K_{D\text{-}DO}$ for the high EtOH concentration range were the same as those obtained without added H_2O_2, suggesting that the contribution of H_2O_2 toward photocatalytic EtOH oxidation might be negligibly small at high EtOH concentration.

Considering the above results, the reaction mechanism that contributed to H_2O_2 production appears to differ for the two EtOH concentration ranges.

3.5. O_2 production by TiO_2 photocatalytic oxidation with H_2O_2

As stated above, H_2O_2 contributed the oxidation of EtOH in the low EtOH concentration range. Therefore, H_2O_2 is oxidized and reduced during photocatalysis as described in Eqs. (29), (30) and (7) as well as the reduction of H_2O_2 to H_2O (Eqs. (31–33)) [5,7–9,37–43] and the ratio of progress for these two sets of reactions is 1:1 [45].

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \quad (31)$$

$$OH^\bullet + e^- \rightarrow OH^- \quad (32)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (33)$$

To verify this H_2O_2 reaction ratio on photocatalysis, we measured the amount of DO produced from oxidation of H_2O_2 in the absence of EtOH.

Fig. 7 shows the changes of DO concentration obtained when 0.01–0.1 mM H_2O_2 was added before UV irradiation. The increase of DO concentration was observed immediately upon subjecting the suspension to UV irradiation and then the concentration of DO decayed slowly during the irradiation process. The r_{DO} value obtained from photocatalysis at each concentration of H_2O_2 was almost the same as that obtained from photocatalysis without added H_2O_2.

Next, the increasing DO production rate in Fig. 7 was estimated, and the concentration of DO produced was calculated from the rate and plotted as a function of H_2O_2 concentration, as shown in Fig. 8. The concentration of DO produced gently increased with increasing H_2O_2 concentration. Though the concentration of DO was an averaged value, the DO consumption in the DO increment range was assumed to be negligible because r_{DO} is very small, as seen in Fig. 8. The O_2 production ratio, defined as (O_2 production)/(concentration of H_2O_2 added), is

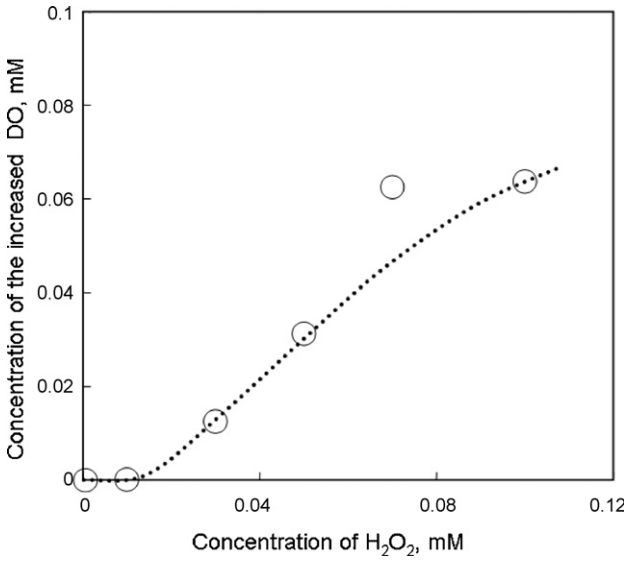


Fig. 8. DO concentration observed during photocatalysis of TiO_2 suspensions containing 0.1 mM H_2O_2 and no EtOH. The concentration was estimated from the increased rate of DO production observed in Fig. 7.

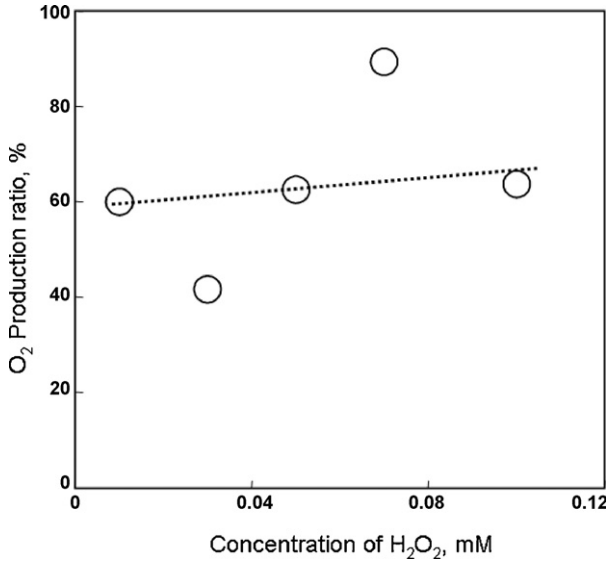


Fig. 9. Production ratios for O_2 as a function of H_2O_2 concentration.

shown in Fig. 9 for varying H_2O_2 concentrations. We found that approximately 63% of the H_2O_2 was oxidized to O_2, and we assumed that the remaining 37% was reduced to H_2O. The reduction ratio of H_2O_2 was smaller than its oxidation ratio, indicating that reduction of O_2 occurred.

4. Discussion

4.1. Relationship between $K_{D\text{-}DO}$ and the mechanism of the TiO_2 photocatalytic reaction

At the low EtOH concentration range, $K_{D\text{-}DO}$ was large, and increasing concentrations of acetaldehyde and formaldehyde were observed. These results suggest that the oxidation of EtOH and acetaldehyde (Eqs. (13–20)) proceeded more readily with increasing concentrations of EtOH. By contrast, in the high EtOH concentration range, $K_{D\text{-}DO}$ decreased to 0.1 times the value observed for the lower EtOH concentration range and the concentration of acetaldehyde increased, whereas that of formaldehyde decreased. Inhibition of the reaction (15) with increasing the concentration of EtOH indicates that the concentration of CH_3COOH at the surface and the production of CO_2 are decreased. Hence the mineralization to consume DO become small and the $K_{D\text{-}DO}$ decreased as mentioned in Section 3.1.

H_2O_2 was major produced as an intermediate during the photocatalytic oxidation of EtOH. Other groups have reported that H_2O_2 is mainly produced from the photocatalytic oxidation of EtOH through Eqs. (21)–(23) [13]. The reaction rate constant associated with Eq. (23) is very slow ($k = 10\ M^{-1}\ s^{-1}$), indicating that the intermediate radical $CH_3CH(OH)OO^{\bullet}$ has to react with CH_3CH_2-OH before reacting at the surface of TiO_2 to produce $CH_3CH{=}O$ and $O_2^{\bullet -}$ [13]. Considering this reaction pathway, the chain reaction proceeded more readily at high EtOH concentrations, whereas at low EtOH concentrations, H_2O_2 production may occur through the reduction of O_2 as depicted by Eqs. (25)–(27) and as stepwise carried out the reactions (21)–(23).

4.2. Effect of H_2O_2 addition on photocatalysis at low concentrations of EtOH

At low EtOH concentrations, $K_{D\text{-}DO}$ increased upon the addition of H_2O_2 to the TiO_2 suspension, indicating that the photocatalytic oxidation of EtOH was accelerated by H_2O_2.

As shown in Fig. 6, an increase in DO was observed for EtOH concentrations of 0.1–7 mM, and the DO production kept on each period time for several minutes. If 0.1 mM H_2O_2 was completely oxidized to O_2 at each EtOH concentration, then the starting time for the decay of DO production should be delayed by increasing the concentration of EtOH. However, the observed delay shortened with increasing EtOH concentrations, indicating that the oxidation of intermediates was carried out more readily than the oxidation of H_2O_2 to O_2. Furthermore, a slight decrement of r_{max} was observed when H_2O_2 was added to the TiO_2 suspension at lower EtOH concentrations. Since r_{max} was defined as the total of the O_2 consumption and reproduction rates constant [31], O_2 production from the oxidation of H_2O_2 caused a decrease in r_{max}. However, the small difference between r_{max} values observed with and without H_2O_2 also indicates that EtOH and intermediates was more readily oxidized than H_2O_2. Based on the suggestion, we can expect that the production of oxidative active species such as $HO^{\bullet}$ (Eq. (31)), Ti–$O^{\bullet}$, and Ti–$^{\bullet}OH$ (Eq. (34)) may be accelerated by accelerating the oxidation of EtOH (Eq. (35)):

$$H_2O_2{-}Ti + e^- \rightarrow Ti{-}O^{\bullet}\ (\text{or}\ Ti{-}{}^{\bullet}OH) + OH^- + H^+ \quad (34)$$

$$Ti{-}O^{\bullet}\ (\text{or}\ Ti{-}{}^{\bullet}OH) + CH_3CH_2OH\ (\text{or intermediates}) \rightarrow CH_3CH^{\bullet}OH\ (\text{furtheroxidation}) \quad (35)$$

Without addition of EtOH, the 63% of H_2O_2 was oxidized to O_2 as shown in Fig. 9. When the almost all of h^+ photo-induced is reacted with EtOH and intermediate, the photocatalytic reduction of H_2O_2 as Eqs. (31) to (33) is accelerated.

In addition, the reaction of H_2O_2 and $CH_3C^{\bullet}{=}O$ (Eq. (36)) may be also carried out, and this reaction is effective in the low EtOH concentration range:

$$H_2O_2 + CH_3C^{\bullet}{=}O \rightarrow CH_3COO^- + OH^{\bullet} \quad (36)$$

Hence, we suggest that H_2O_2 was effective to oxidize EtOH for increasing $K_{D\text{-}DO}$ value in low EtOH concentration range.

4.3. Effect of H_2O_2 addition on photocatalysis at high concentrations of EtOH

At high EtOH concentrations, r_{max} and $K_{D\text{-}DO}$ were not changed by the addition of H_2O_2. These results can be explained by assuming that the amount of H_2O_2 adsorbed at the surface decreased as the EtOH concentration increased. In fact, others have reported that H_2O_2 and EtOH adsorb at Ti^{4+} sites on the surface of TiO_2 [14,15,38,41,42,44,46]. Furthermore, since a high concentration of H_2O_2 has been measured in the supernatant after removal of TiO_2 powder in previous TiO_2 photocatalysis studies using sacrificial reagents [38,39], H_2O_2 may be not adsorbed at the surface or displaced by a sacrificial reagent and dispersed into the bulk solution because of the high concentration of EtOH and an intermediate than H_2O_2. Hence, we suggested that at high concentration of EtOH, the concentration of EtOH and intermediate adsorbed at the surface were higher than that of H_2O_2.

Notice here that H_2O_2 might be reduced during TiO_2 photocatalysis even at high EtOH concentration. Since the conduction band e^- is increased with oxidizing EtOH as have been known for current doubling effect [6,46], the photocatalysis with EtOH accelerates H_2O_2 reduction to produce water as Eqs. (31)–(33). We assumed that the oxidation of H_2O_2 as Eqs. (29) and (30) may be ruled out at high EtOH concentration region because the concentration of EtOH and an intermediate is much higher than that of H_2O_2. Hence, we suggested that the increase of adsorption of EtOH and an intermediate and the decrease of H_2O_2 at the surface as the displacement may major reason for no positive effect of H_2O_2 addition on photocatalytic oxidation of EtOH.

The production of $HO^\bullet$ from H_2O_2 via photolysis has also been reported [9]. However, under the present experimental conditions, r_{max} and $K_{D\text{-}DO}$ were not affected by the addition of H_2O_2 at high EtOH concentrations, indicating that the photolysis of H_2O_2 might be negligible at these concentrations and that Eqs. (34) and (35) might be the major reactions accelerating EtOH oxidation.

4.4. Behavior of O_2 and H_2O_2 produced from TiO_2 photocatalysis with EtOH

The production mechanism of H_2O_2 is explained by considering Eqs. (25)–(27) as photocatalytic reduction of O_2, and then O_2 firstly must be reduced to $O_2^{\bullet-}$. Oxygen molecules have been reported to adsorb at Ti^{3+} or Ti^{4+} sites [25–27], suggesting that the steady-state amounts of $O_2^{\bullet-}$ and O_2 decrease with increasing amounts of EtOH. On the basis of these suggestions, we expected that the behavior of O_2 and $O_2^{\bullet-}$ in photocatalysis with EtOH was directly related to that of H_2O_2 observed in this study [31].

For 0.1–1 mM EtOH, the H_2O_2 was produced and the concentration increased as shown in Fig. 5. In fact, in our previous work in Ref. [28], the increase in the concentration of $O_2^{\bullet-}$ was observed in the 0.1–1 mM of EtOH concentration range as a result of the acceleration of O_2 reduction [31]. Then Eqs. (25)–(27) might be accelerated to produce H_2O_2.

As shown in Fig. 5, for 1–5 mM EtOH, production of H_2O_2 reached plateau. As have been shown in our previous work in Ref. [31], for 1–10 mM EtOH, the concentration of $O_2^{\bullet-}$ decreased slowly, suggested that $O_2^{\bullet-}$ might react with EtOH and intermediate as the chain reaction through Eqs. (37) and (38) known as Russell-like reactions [47] with competing with displacing from O_2, $O_2^{\bullet-}$ to EtOH and accelerating the reactions (25)–(27).

$$O_2^{\bullet-}\,(HO_2^-) + CH_3CH_2OH\,(CH_3CH{=}O) \rightarrow CH_3CH^\bullet OH\,(CH_3C^\bullet{=}O) + HO_2^-\,(H_2O_2) \quad (37)$$

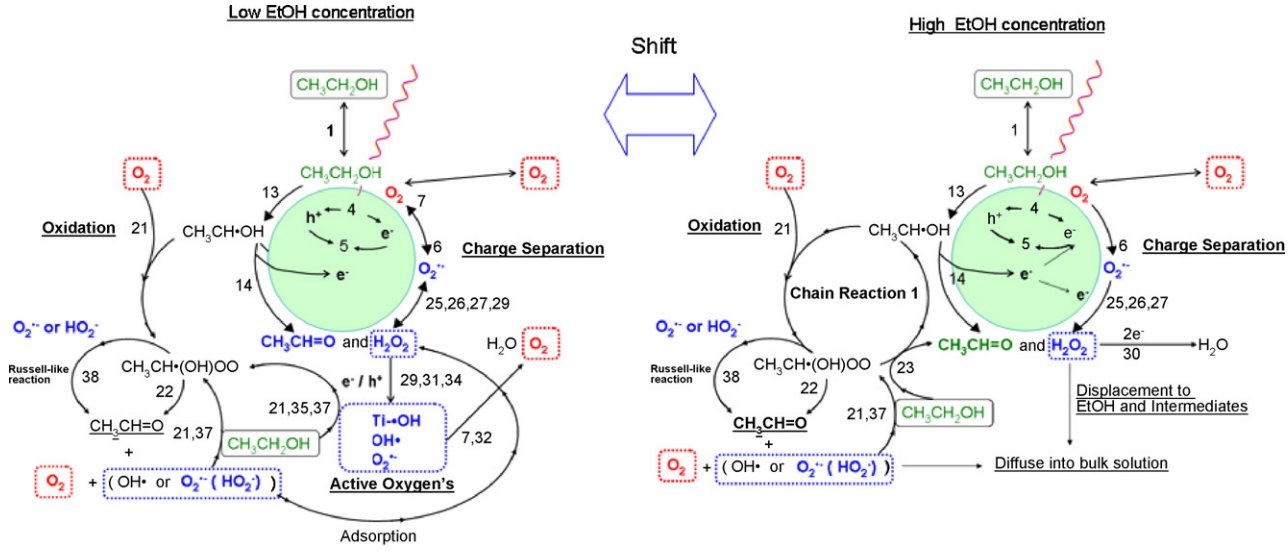
$$CH_3CH(OH)OO^\bullet + O_2^{\bullet-}\,(HO_2^-) \rightarrow CH_3CH{=}O + O_2 + (OH^\bullet \text{ or } O_2^{\bullet-}/HO_2^-) \quad (38)$$

At higher EtOH concentrations than 10 mM, the concentration of $O_2^{\bullet-}$ was significantly decreased in the previous work [31]. This result could be explained by considering the decreasing amount of O_2 adsorbed at the surface and the accelerating multi-reduction of O_2 to produce H_2O (and/or Ti–OH) through Eqs. (31)–(33).

As stated above, the behavior of H_2O_2 produced in TiO_2 phtocatalysis with EtOH is consistent with the observation that the behavior of $O_2^{\bullet-}$ produced in TiO_2 phtocatalysis with EtOH [31]. The plausible reaction mechanism proposed in the present study is summarized in Scheme 3.

5. Summary

In the present study, we demonstrated that the mechanism of the photocatalytic reaction of EtOH can be analyzed by monitoring the O_2 and H_2O_2 produced and consumed during the reaction. The consumption process of DO could be analyzed with



Scheme 3. Plausible reaction mechanism for EtOH decomposition at both low and high EtOH concentrations.

Langmuir–Hinshelwood kinetics. In the present study, the parameter $K_{D\text{-}DO}$ calculated from L–H kinetics was defined as (O_2 consumption rate constant)(O_2 reproduction rate constant)$^{-1}$, indicating that a large $K_{D\text{-}DO}$ reflects a more irreversible O_2 consumption with progressing photocatalytic oxidation of EtOH.

The $K_{D\text{-}DO}$ value for the low EtOH concentration range (0.1–5 mM) was 10 times as high as the $K_{D\text{-}DO}$ values observed for high EtOH concentrations (10–50 mM). Furthermore, by addition of 0.1 mM H_2O_2, the $K_{D\text{-}DO}$ was increased in the low EtOH concentration range, whereas the addition of H_2O_2 did not affect $K_{D\text{-}DO}$ at high EtOH concentrations. In the results obtained from HPLC and starch–Iodine methods to measure intermediates such as acetaldehyde, formaldehyde, and H_2O_2, production of larger amounts of acetaldehyde and H_2O_2 were observed as the EtOH concentration increased, whereas the amount of formaldehyde decreased at high EtOH concentrations. These results indicate that further photocatalytic oxidation of acetaldehyde occurred in the lower ethanol concentration range, but that the reaction might cease at high EtOH concentrations till the concentration of acetaldehyde increased to higher than EtOH. Because the oxidation of acetaldehyde consumes large amounts of O_2, these results and the speculated reaction mechanism determined from the HPLC and I–starch methods supported the $K_{D\text{-}DO}$ results obtained for the photocatalytic oxidation of EtOH and H_2O_2.

The detailed contribution of H_2O_2 to TiO_2 photocatalysis was also studied and appeared to be affected by the concentration of EtOH. In the low EtOH concentration range, oxidative radical species similar to $OH^{\bullet}$, such as Ti–$^{\bullet}$OH and Ti–O$^{\bullet}$, that might be produced by photocatalytic reduction of H_2O_2 appeared to be critical for the oxidation of EtOH. However, at high EtOH concentrations the contribution of H_2O_2 was negligible, suggesting that increasing amounts of EtOH displaced the H_2O_2 adsorbed at TiO_2 surface and that a reduction of H_2O_2 to produce H_2O might be accelerated. Because the oxidation EtOH intermediates may proceed more readily than that of H_2O_2 to produce O_2, the reaction of reactants with $O_2^{\bullet-}$ produced from the oxidation of H_2O_2 may be ruled out.

In the absence of EtOH, approximately 63% of O_2 and 37% of H_2O species are produced from photocatalytic reactions involving H_2O_2. H_2O_2 reduction was relatively small because of the competing O_2 reduction process.

As demonstrated in this study, this method permits the elucidation of photocatalysis reaction mechanisms by monitoring O_2 and reactive oxygen species. This method is a powerful tool for obtaining information about photocatalytic reactions and could be applied in the treatment of wastewater.

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(d) In our study, CH_3COOH could not be measured. We supposed the reason that the concentration of CH_3COOH that dispersed into bulk solution was too low to be detected by HPLC. In fact, the strong adsorbability of CH_3COOH onto the metal oxide surface as TiO_2 [34(a)–(c)].
[35] Generally, the rate of I^{3-} formation could distinguish between the H_2O_2 and other organic peroxide such as R-OOH which is produced by photocatalysis with EtOH because of the different reaction rates. However, in our study, the differences could not be distinguished. Furthermore, the organic peroxide slowly reacts with I^{3-} to produce some products and the products might have broad absorption that we observed in this study (the spectra was not shown here). If H_2O_2 would be produced at high EtOH concentration region, it would be not higher than 10 μM based on the results of Fig. 5. The reason is that H_2O_2 production is limited by the concentration of DO in closed system in the present study.
[36] In our study, every experiment was carried out in alkaline condition at pH of 11.5. This condition was intentionally corresponding to previous our work as Ref. [31]. Then the molecular ratio HO_2^-/H_2O_2 is 0.6 in the alkaline solution of pH 11.5.
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